RATE STUDIES ON MONOETHANOLAMINE-CARBON DIOXIDE-WATER SYSTEM

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
In
Chemical Engineering

Submitted By
Ratnakar Patra
110CH0398

Under the guidance of

Dr. MADHUSHREE KUNDU

Department of Chemical Engineering
National Institute of Technology
Rourkela

2013-14

National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "**RATE STUDIES ON METHANOLAMINE-CO_2 -WATER SYSTEM"**, submitted by **Mr. Ratnakar Patra, Roll no. 110CH0398**, in partial fulfillment of the requirements for the award of degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the report has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date:

Place: Rourkela

Dr. Madhushree Kundu

Department of Chemical Engineering

National Institute of Technology

Rourkela – 769008

ACKNOWLEDGEMENT

I express my sincere gratitude to **Prof. M.Kundu** for providing me an opportunity to work on this project and for her constant guidance and timely suggestions throughout. I am also thankful to **Prof. H.M.Jena** (Faculty Advisor) and **Prof. R.K.Singh** (Project Co-ordinator) for their valuable guidance and advice.

Finally I thank my parents and friends for their support and encouragement without which this project would not have been possible.

Date:

Ratnakar Patra

110CH0398

Department of Chemical Engineering

National Institute of Technology, Rourkela

ABSTRACT

Owing to the increase in Green House Gases in the atmosphere, the most widely known Global Warming, in the present scenario, is inevitable. Thus, to mitigate the comparatively larger amount of these gases, various scientific and technological developments have been ensured. Carbon Capture & Storage (CCS) technique helps in this regard to lessen the amount of CO_2 in the atmosphere by absorbing CO_2 in a suitable absorbent and then stripping it from that absorbent in the subsequent process to get almost pure CO_2, which is stored and used for its many industrial applications. Amongst the sources of CO_2, Natural Gas Power Plant, Coal-fired Power Plant and Nuclear Power Plant are of prime concern to subject our problems and project a solution. Although having a different prospects and methods of CO_2 capture, CCS by Chemical Absorption Method (Post-Combustion) can be viewed as a commercial approach to have a large scale application.

For this, although a large number of solvent along with their blends has been experimented, a systematic theoretical as well as realistic practical approach on many of the solvent and the comparison between them has yet not been performed. Again, where many of the literature review shows VLE studies on the respective solvents; very few of them have revealed a significant approach on Rate Studies. This thesis is about ensuring a more practical approach to determine the performance of the solvent MEA (Monoethanol Amine) in CO_2 absorption in Rate Model using ASPEN PLUS.

Table of Contents

LIST OF FIGURES

LIST OF TABLES

CHAPTER-1

INTRODUCTION

The rise in atmospheric temperature especially during last three decades has compelled our science and technology to go deeper to find a reasonable and permanent solution. The aura started with the technology of Greenhouse mitigation, which was recognised as the prime factor for the instability of the atmosphere. Amongst the greenhouse gases, the CO_2 content is one of the most vital causes of the Global Warming. Thus, Greenhouse gas mitigation technology on basis of CO_2 capture is being practised in industrial scale. As far as the sources of these emissions are concerned, recent data showed that in US, energy oriented CO_2 emissions contributed a 98% of the total emissions in 2007, with the electricity generation contributing a 40% [1]. These greenhouse gases evolved during the combustion of the fossil fuels facilitate sunlight to enter the atmosphere freely. When the sunlight strikes upon the Earth, some of it is reflected back into space as infrared radiation (heat). These greenhouse gases absorb a portion of that infrared radiation and reemit it back to the Earth. This effectively raises the temperature of the Earth [25].

Carbon Capture & Sequestration (CCS) is the process involving capture and long-term storage of atmospheric CO_2. It generally refers to:

- The removal of CO_2 from atmosphere and depositing in a reservoir.
- The removal of CO_2 from flue gases and storing it in an underground reservoir.

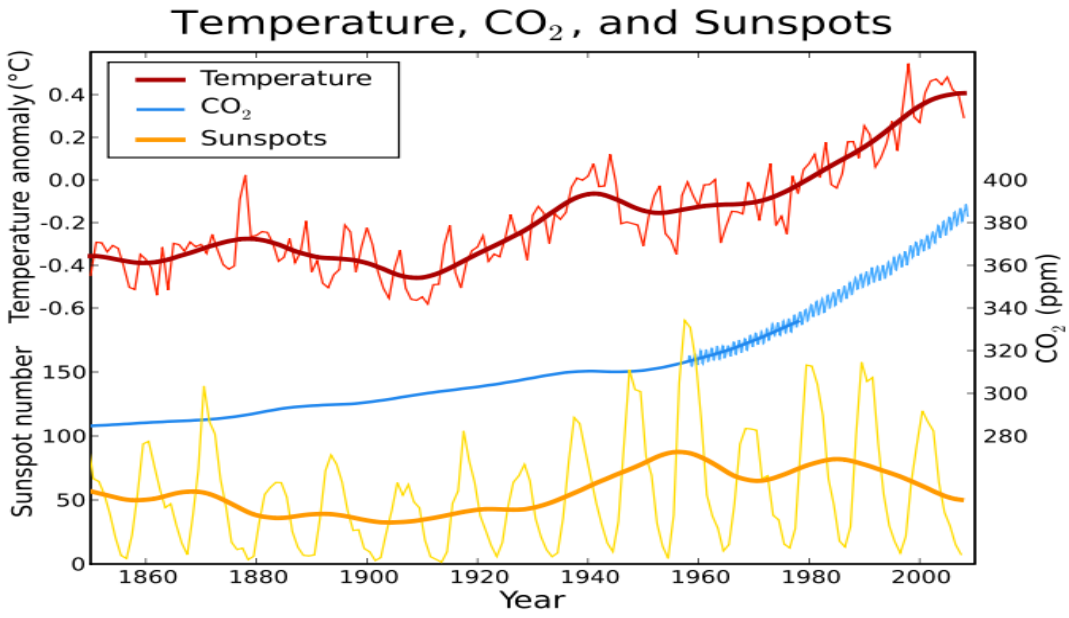

Figure 1.1: The variation of CO_2, temperature and sunspots from year 1860-2000 [25]

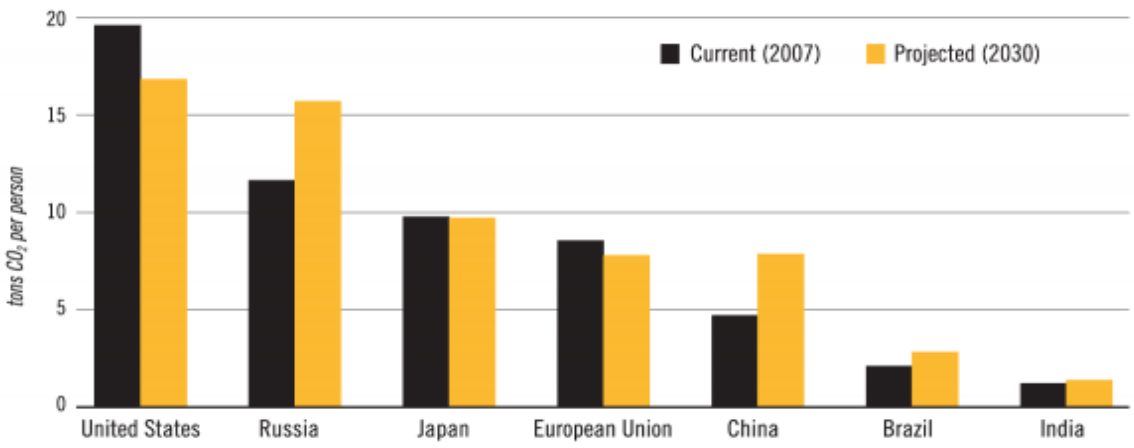

Figure 1.2: The current and projected value of CO_2 per person in several countries.

1. METHOD OF CO_2 SEQUESTRATION

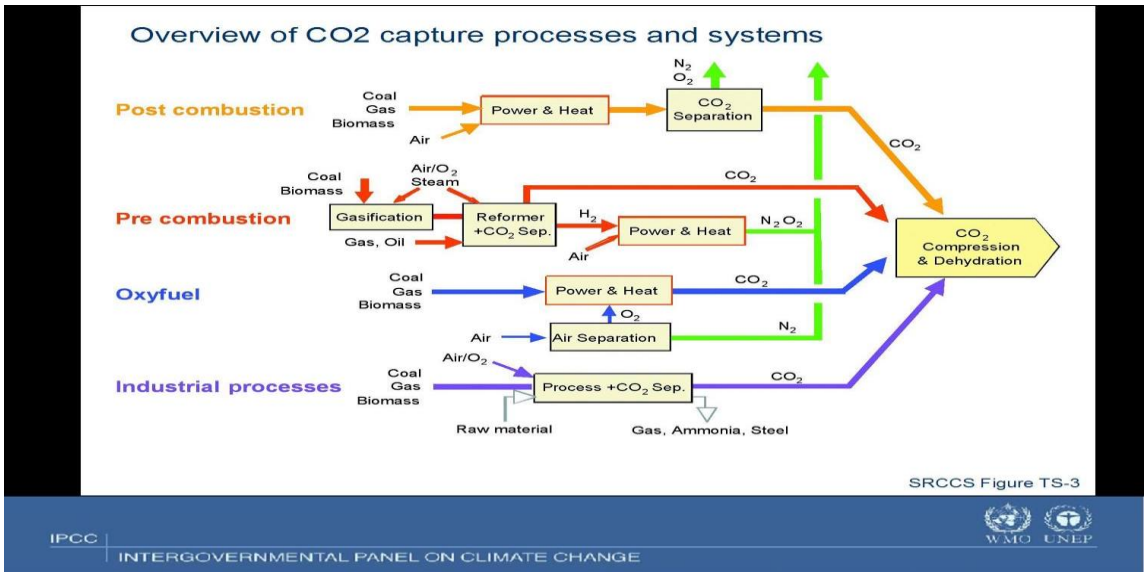

Figure 1.3: Different methods of CO_2 sequestration

1.1. Post Combustion Capture

Being a downstream process equivalent to the flue gas desulfurization process, Post-combustion capture involves CO_2 removal that are present in the flue gas produced after the combustion. Due to the application of air as the oxidant, the flue gases tend to be diluted with nitrogen. Also, as the flue gases are at 1 atm pressure, a large quantity of gas has to be treated.

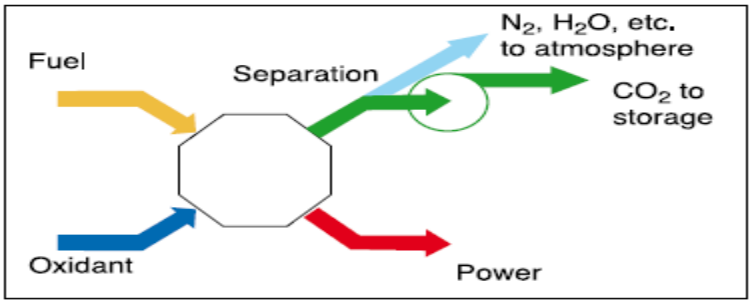

Figure 1.4: Schematic of post-combustion capture [25]

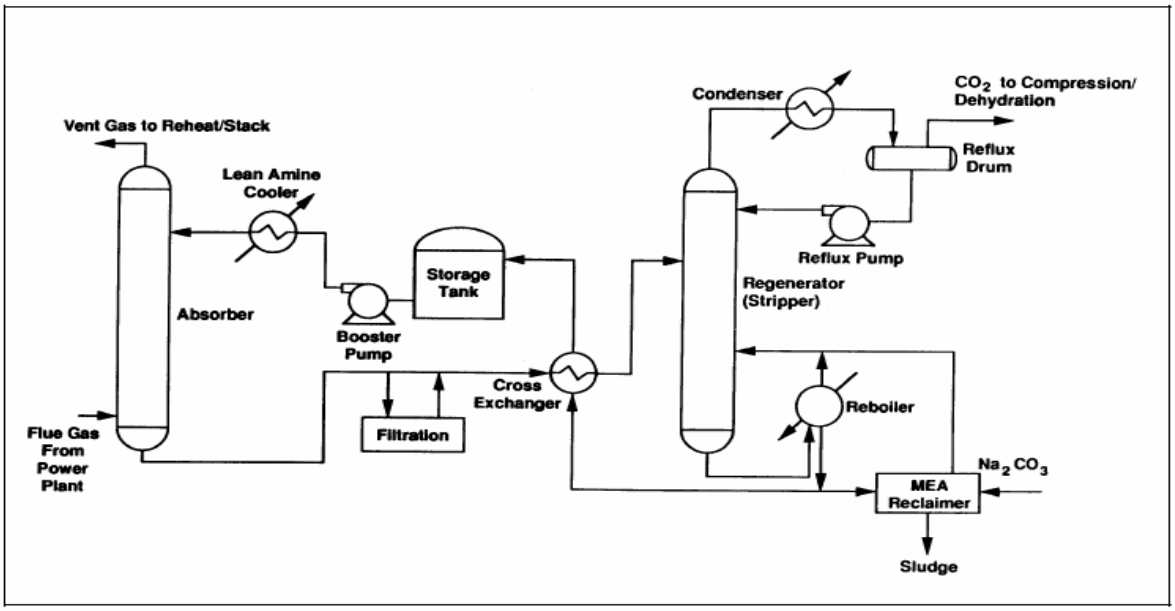

Fig. 1.5: Process flow diagram for the post-combustion CO_2-capture process using MEA solvents [25]

Post-combustion capture methods:

- Chemical absorption
- Physical absorptions
- Membrane separation
- Adsorption
- Cryogenic separation

1.2. Oxyfuel combustion

The dilution effect due to the presence of Nitrogen reduces the Calorific Value of the flue gas in case of the Post Combustion Process. To counter this problem, Oxyfuel technique is used where in stead of air, only O_2 is provided for the combustion process. However, there is no provision to remove the fuel bound N_2 [6] in this process, for which steps need to be carried out prior to the combustion to avoid excess N_2 and excess sulphur

and nitrogenous compounds as well. As the reaction involved exhibits a high heat of reaction, the temperature of the system needs to be controlled.

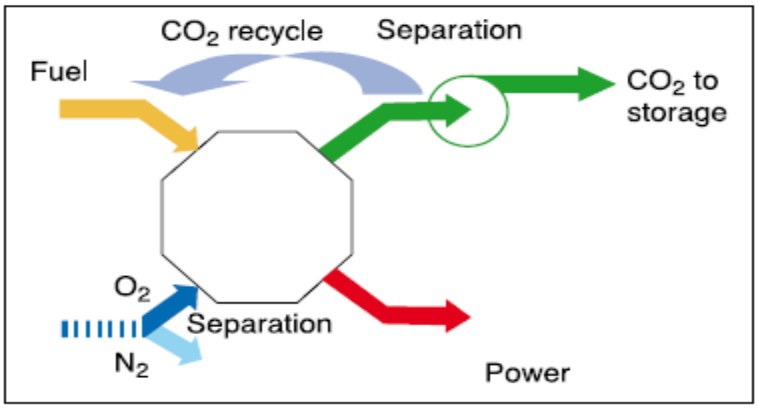

Figure 1.6: Schematic of oxyfuel combustion

1.3. Precombustion capture

The carbon content of the fuel often tends to choke the equipments, nozzles by creating a trace bed on the path. If the temperature is not uniform and optimal, then severe problem may occur. Thus, prior to combustion, the carbon content of the fuel is mitigated in this process which is useful to generate electricity.

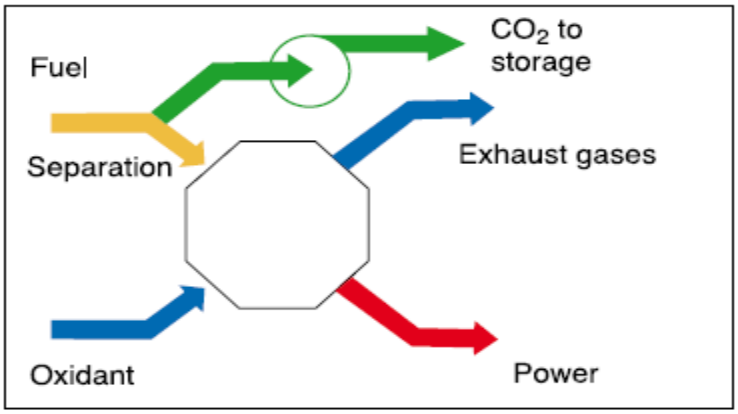

Figure 1.7: Schematic of precombustion decarbonization.

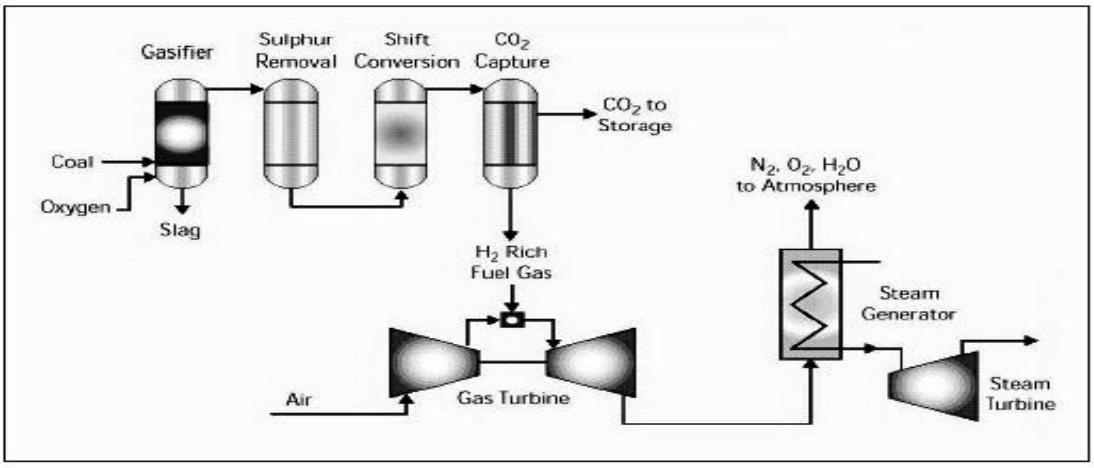

Fig. 1.8: Process flow diagram for the pre-combustion CO_2-capture process.[25]

Coal and O_2 is subjected to the gasifier to produce syngas which is then processed for sulphur removal. The excess CO is then sent to the shift converter to convert it to CO_2, which is captured in an absorber. The remaining flue gas is sent to a gas turbine and steam turbine successively to generate electricity. The removal of impurities prior to the electricity generation process makes IGCC the most environment friendly technique till date.

2. SOURCE OF CO_2 & SOLVENT SYSTEMS

2.1 Structure of different types of Solvents

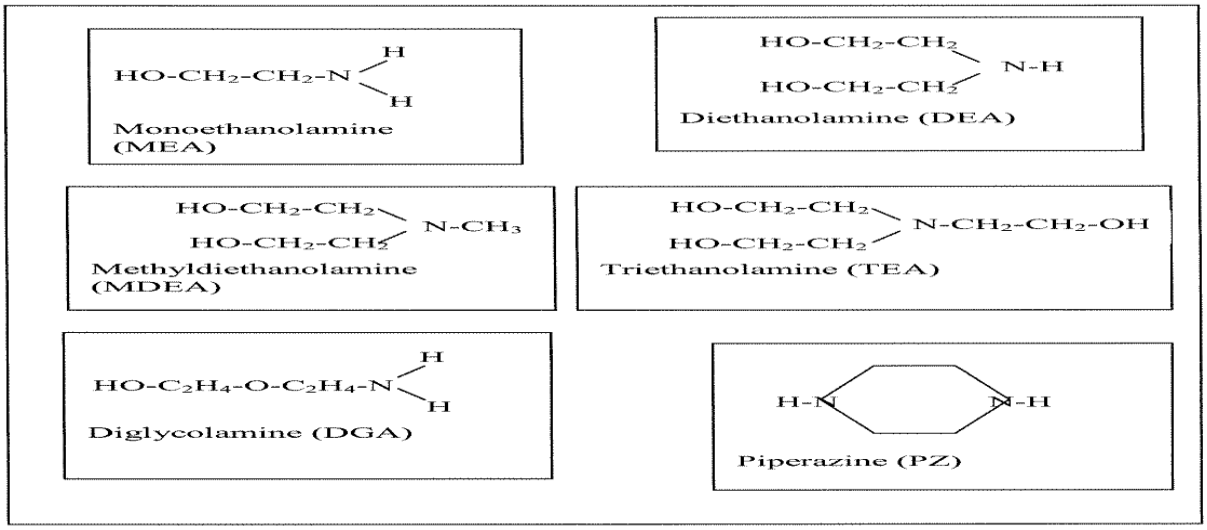

Figure 1.1. Chemical structures of most common alkanolamines.

Figure 1.9: Chemical Structure of most common Alkanolamines

2.2. Different Source of CO_2 emission in Flue gases

Table 1.1: CO_2 partial pressure in flue gases of different combustion systems. [25]

Flue gas source	CO_2 concentration, % vol (dry)	Pressure of gas stream, MPa	CO_2 partial pressure, MPa
Natural gas fired Boilers	7-10	0.1	0.007-0.01
Gas turbines	3-4	0.1	0.003-0.004
Oil fired boilers	11-13	0.1	0.011-0.013
Coal fired boilers	12-14	0.1	0.012-0.014
IGCC after Combustion	12-14	0.1	0.012-0.014
IGCC synthesis gas after gasification	8-20	2-7	0.16-1.4 (before shift)

3. OBJECTIVE OF THE THESIS

The objective of this thesis is to determine the Optimal Operating Conditions and Constraints for CCS system.

4. SCOPE OF THE WORK

- To concentrate on NGCC or IGCC power plants and the respective CO_2 emission
- To perform a Rate Studies for CO_2 absorption in ASPEN PLUS by taking the help of some literature data.
- The operating constraints are to be set based on the appropriate Design Specification

- Sensitivity Analysis is to be performed to analyse the dependency of the result with the change in different manipulated variables.
- Finally, taking the result, graph is to be plotted and the nature of the plot is to be examined to have a clear idea regarding the phenomena occurring throughout the system.

5. CHAPTER LAYOUT

- **CHAPTER-1:** Giving an introductory preview on the CCS process, this chapter explains various processes that are adopted for the Sequestration of CO_2 and also shows the amount of CO_2 present in the different plant emissions.
- **CHAPTER-2:** This chapter presents the literature survey on the development of CO_2 sequestration process along with the gradual progress on use of different Amine Solvents. It also explains various modelling aspects including the ENRTL model for the purpose.
- **CHAPTER-3:** This chapter describes the process of CCS occurring in a chemical plant with detailed steps in this regard. It also emphasises on the Chemistry of different reactions takes place in the process along with the pre-requisite Thermochemistry data in addition to the reaction mechanism.
- **CHAPTER-4:** This chapter explains the various modelling used for the Simulation purpose with the specific advantages. It again focuses on the ASPEN Rate Sep Analysis along with the typical fast reactions kinetics and the Film Discretization.
- **CHAPTER-5:** This chapter reveals the actual Design and Simulation based on my work including various controlling parameters, Input Specifications, Design Specifications and Sensitivity Analysis etc.
- **CHAPTER-6:** The results obtained during the Simulation process has been contained in Tabulated form along with constructing the plots for respective data tables, in this chapter. It also reported the discussion on the nature of these plots.
- **CHAPTER-**7: This chapter ends the project work with a conclusion and states the future recommendation of this work.

CHAPTER - 2

LITERATURE REVIEW

Various available technologies for CO_2 capture from power plants are there but a number of them are still in development stages which are to be optimised. For flue gas, a chemical solvent such as ME or a solid sorbent such as solid phase amine, AgO or LiH is preferred. For high CO_2 concentration i.e. from Natural gas , a physical solvent is preferred. Also for high temperature separation, Adsorption by using a high surface area adsorbent such as Zeolite, Alumina or activated carbon, Cryogenic distillation by liquefaction and purification of CO_2, Gas separation membranes using solubility selective polymer for low temperature separation and ceramics are used. Advanced process such as CO_2 capture by an ionic liquid and a high pressure CO_2 separation process in an IGCC plant are also being investigated by researchers.[25]

However, Chemical absorption has advantages over Physical absorption due to: (a) Low Capital & Capital Cost (b) Less Energy Consumption. Meisen et.al. showed the problems of corrosion and foaming in the absorption process. The adsorption method (PSA, TSA) used in 1997 is relatively simple, but unsteady state operation, low selectivity, low capacity. The stripper top condenser is necessary to ensure a small and gradual temperature gradient through the column.

The University of Regina has an absorption/stripping pilot plant which obtains CO_2 from the combustion of natural gas. The absorber has a 10 cm diameter. This absorption unit has been used to analyse mass transfer performance for various gas and liquid flow rates, CO_2 partial pressures, liquid temperatures, solvent concentration, solvent type and packing. The pilot plant has also been used to quantify the heat duty of CO_2 capture using 30 wt% MEA and other solvents. Reasonably long test periods can be conducted to quantify operational problems such as solvent degradation, levels of heat-stable salts, and corrosion . The system also facilitates the analysis of the heat duty under typical industrial operating conditions . Korea Electric Power and Mitsubishi Heavy Industries have also performed CO_2 capture pilot plant studies using aqueous MEA solutions. CO_2 Absorption Rate and Solubility analysis in Monoethanolamine/Piperazine/Water [7] was determined at different conditions. Degradation of MEA [8] in the absorption process in a coal fired power plant was studied and it was found that acetylated MEA is the major constituent. A survey on the CO_2 capture technologies from power plant [9] showed that the capture technologies contribute a significant cost factor in the total process.

A conceptual process flowsheet for a pulverized coal steam boiler operating on a supercritical steam cycle with CO_2 capture has been developed [10]. It has been found that the overall thermal efficiency on a LHV basis is reduced from 44.2% to 35.4%. For oxyfuel

combustion to be incorporated, some modifications to the burner design are required. In addition, lines for recirculation of the CO_2 need to be provided. One of the other challenges is the lower purity of CO_2 produced in Oxyfuel combustion. For the production of ultra-pure CO_2 (matching that produced in an amine absorption process), additional distillation steps would have to be added after the inert gas removal steps [11]. In order to understand the issues associated with the operability, startup and shutdown of these systems, demonstration plants employing oxyfuel combustion in boilers have to be commissioned. Recently, Vattenfall commissioned a 30MWth pilot plant facility for a detailed testing of the oxyfuel firing facility [12]. Design of new plants operating on a supercritical steam cycle can be considered since these plants inherently have a higher efficiency. For oxyfuel combustion to be incorporated in gas turbines, it is necessary that the technical and operational feasibility of turbines capable of operating on CO_2 as the main working fluid be demonstrated. A critical technology that needs to be improved for oxyfuel combustion to be more efficient is the air separation unit. Current cryogenic air separation plants are showing improvement in efficiency due to improved compressor efficiencies and larger scale plants. It is necessary to optimize this further. Ion transport membranes which may offer more efficient separation of O_2 from air are presently under development [13]. Chemical looping combustion systems are a relatively new technology and are still in the development and pilot plant stage. In chemical looping systems, the research focus needs to be on developing better attrition resistant metal oxide carriers which have other desirable characteristics such as high rate of reaction. The thermal stability of these particles needs to be enhanced and their integrity in pressurized environments needs to be preserved if chemical looping systems are to be integrated efficiently with gas turbine power generation cycles. In addition, the compatibility of chemical looping systems with coal needs to be explored. Gasification systems represent an attractive option since they allow us to obtain syngas and electricity from coal. However, the capital cost of the equipment is very high. The complexity of the system makes it difficult to operate and hence, the availability of these systems cannot be guaranteed. [14].

Chemical absorption is a downstream process and is very similar to flue gas desulfurization and other end of the pipeline solutions. A pilot plant has been set up as part of the CASTOR project at the Esjberg Power Station operated by Eslam in Denmark [15]. This unit is designed to capture 1 tonne CO_2 / hour. The hands on experience gained from this trial will help in gaining a better understanding of the technology. In addition, other demonstration projects such as the collaboration between Alstom and AEP in West Virginia are already

underway [16]. The plant operates with the chilled ammonia solvent and operation of the CO_2 capture system has commenced recently.

In order to optimise the CO_2 removal system, the parameters that affect absorber and desorber operation would be adjusted to improve performance and efficiency. These parameters are flue gas temperature, lean solution temperature, CO_2 loading, lean solution flow rate. Desideri showed that when temperature of lean increases, flue gas temperature in the absorber and thereby flue gas temperature at the top of the vessel increases.[25] Separation of CO_2 from flue gas generated by power plant using present day technology is expensive . For a 20% improvement in the energy efficiency of chemical absorption, cost is reduced by only 10-12%.

A number of solvent systems have been proposed and studied for CO_2 capture by chemical absorption. MEA has been the most widely studied system with a number of researchers developing flowsheet models to study its performance [18]. Other amines that have been studied include tertiary amines such as MDEA [19]. Sterically hindered amines such as AMP have also been investigated [20]. The performance of hindered amines was found to be better suited to absorption in higher CO_2 partial pressure atmospheres (8-15% CO_2) [20]. Mixed amine blends are designed to take advantage of the desirable properties in primary and tertiary amines. Particular interest has been focused on MEA/MDEA and MEA/AMP blends with pilot plant studies having been conducted [21]. Investigation on DGA/MDEA blends has also been conducted. Other systems that have been proposed include the potassium carbonate system [22] and using ammonia as a solvent for CO_2 capture [23].

While a number of different systems have been proposed and investigated, very few studies which compare the performance of different systems on a consistent basis have been performed. In addition, it was found that not many studies focused on incorporating the appropriate thermodynamic and rate models in the model development. Hence, it was decided to make these issues the focus of this thesis.

CHAPTER - 3

MONOETHANOLAMINE SYSTEM

3.1. PROCESS DESCRIPTION

The CCS process for CO_2 capture using MEA can be categorised into 3 different sections:

1. Flue gas cooling and compression
2. Absorption of CO_2 and regeneration of solvent
3. CO_2 compression

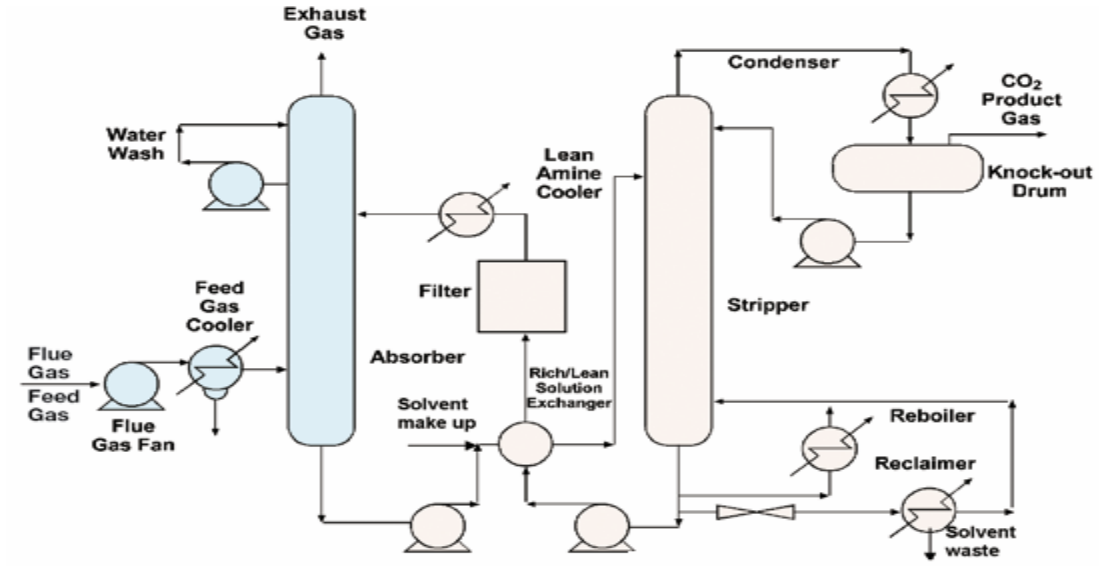

Figure 3-1: Schematic of CO_2 capture by use of MEA solvent [25]

3.1.1 Flue gas cooling and compression:

As the absorber in presence of MEA system has an optimal condition of running temperature around 45°C, the inlet flue gas temperature needs to be kept within the range 40-50°C. For a NGCC plant, the outlet flue gas temperature at the exhaust remains around 110-120°C. Thus to be used in the absorber for the absorption purpose, the low temperature is to be maintained, for which the gas is to be cooled being fed to the absorber unit. For a coal-fired power plant, the exhaust flue gas also requires a cooling system unless it has already been subjected to the wet gas desulfurization scrubber. The cooling system comprises typically of a Direct Contact Cooling tower (DCC), which is basically a packed tower having a counter current flow of cooling water and hot flue gases. The flue gas is fed at the DCC bottom while the cooling water enters at the top. In the process, the flue gas is cooled by evaporation of water which releases the heat content and hence, the water vapour converts into liquid water thereby reducing the water content in the flue gas at the exit of the tower. The comparatively hotter cooling water collected at the bottom is again sent to a cooling

water contact before being recycled to the DCC. The exit flue gas sent to a blower, which especially is a mild compressor in order to have a comparatively high pressure to facilitate the upward flow of gas through the packed absorber. This results in a slight increase in flue gas temperature.

3.1.2 Absorption of CO_2 and regeneration of solvent:

The packed absorber column provides sufficient surface area owing to its nature of packing for CO_2 absorption. The flue gas is subjected at the bottom of the absorber while the lean amine is provided at the top of the absorber. The lean amine enters at a loading of 0.2-0.3 and leaves at a loading of 0.5. In a MEA system, the loading defined on a mole basis [25]:

$$\text{Loading} = \frac{\text{Moles of all } CO_2 \text{ carrying species}}{\text{Moles of all MEA carrying species}} \qquad (3\text{-}1)$$

$$\text{Loading} = \frac{[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [MEACOO^-]}{[MEA] + [MEA^+] + [MEACOO^-]} \qquad (3\text{-}2)$$

Lean amine indicates the amine stream that enters at the top of absorber, which eventually get stripped of the absorbed CO_2 in the stripper. The outlet amine stream, which is absorbed with CO_2, is basically a rich stream. The lean amine is introduced on the second stage with make up water on the 1st stage to operate as a water wash for the removal of the entrained MEA, if any, that may be coming out through the vent along with the vent gas. The make up water also cools the vent gas before allowing it to be released to atmosphere. The rich amine leaving the absorber bottom is carried to the pump before being discharged to a cross heat exchanger, where the absorber bottom rich stream exchanges heat with the desorber lean stream. This results in the heating of the rich stream to attain the required temperature as per the desorber demands where as the lean stream get cooled before being discharged to another cooler to reduce its temperature to the optimal temperature of the absorber as the cooled lean stream will be recycled to the absorber.

The desorber, a typical packed column, consists of a kettle reboiler and is maintained at an elevated pressure (1.8 atm). The preheated rich amine is subjected at the 2nd stage of the desorber and counters the vapours coming from the reboiler as it flows downward. The stream coming out of the top of the desorber is sent to a condenser to condense the water vapour and lower the temperature and next to a flash in order to separate

the CO_2 and H_2O. A part of the flash bottom (pure water) is recycled to the top of the desorber column while an excess water stream is sent to storage. The 1st stage in the desorber performs as a water wash stage to remove the entrained MEA in the vapour leaving the top of the desorber. The heating medium for maintaining the high temperature in the desorber is the steam through the reboiler which produce the heat duty because of three different requirements [25]:

1. Sensible heat to raise the temperature of the rich stream to that in the desorber
2. Heat of reaction to reverse the absorption reaction and release CO_2
3. Heat to produce steam to maintain driving force for transfer of CO_2 from liquid phase to gas phase

3.1.3. CO_2 compression:

The CO_2 removed from desorber requires to be free from moisture and to be compressed before storage in order to avoid corrosion in presence of water molecules. A 4-stage reciprocating compressor is considered with inter stage cooling which discharges the final CO_2 outlet at 90 atm; the liquid CO_2 is then sent to another pump to attain a discharge pressure of 130 atm.

3.2. CHEMISTRY OF MEA SYSTEM

$$2\,H_2O \leftrightarrow H_3O^+ + OH^- \qquad (3\text{-}3)$$

$$CO_2 + 2\,H_2O \leftrightarrow HCO_3^- + H_3O^+ \qquad (3\text{-}4)$$

$$MEA + HCO_3^- \leftrightarrow MEACOO^- + H_2O \qquad (3\text{-}5)$$

$$MEA + H_3O^+ \leftrightarrow MEA^+ + H_2O \qquad (3\text{-}6)$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \qquad (3\text{-}7)$$

3.2.1 Carbamate formation in the MEA system

3.2.1.1 Zwitterion mechanism

Caplow proposed this mechanism in 1968 [10].

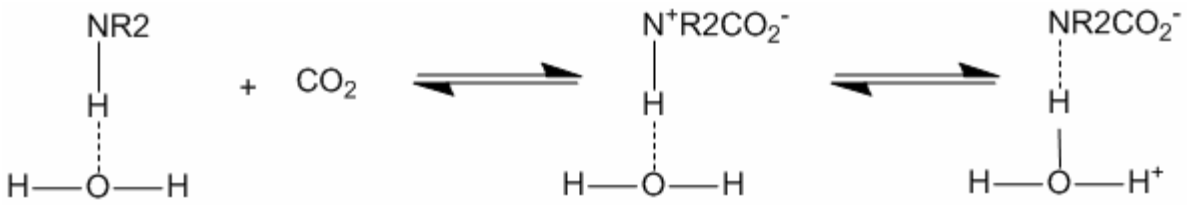

Figure 3-2: Zwitterion mechanism for carbamate formation [25]

Caplow assumed that the amine molecule forms a hydrogen bond with the water molecule before reacting with CO_2. The first step was the formation of an unstable intermediate by the bonding of the CO_2 molecule to the amine. In the second step, the amine proton is transferred to a basic molecule to form the carbamate.

$$CO_2 + R_2NH \longleftrightarrow R_2NH^+COO^- \text{ (zwitterion)}$$

$$R_2NH^+COO^- + R_2NH \longleftrightarrow \underset{\text{(carbamate)}}{R_2NCOO^-} + \underset{\text{(protonated amine)}}{R_2NH_2^+}$$

3.2.1.2 Termolecular mechanism

A single-step Termolecular carbamate mechanism was proposed in 1989.

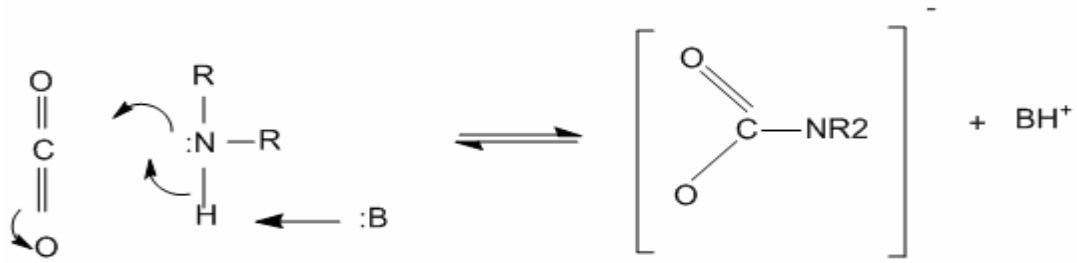

Figure 3-3: Termolecular mechanism for carbamate formation [25]

The bond formation of Amine with CO_2 and proton transfer occurs simultaneously ignoring the formation of hydrogen bond and thus, the lifetime of intermediate is negligibly. However, the termolecular mechanism has more probability to occur due to the fast reaction. Again, for some systems, the zwitterion mechanism provides implausible results [15].

CHAPTER – 4

MODELING DESCRIPTION

4.1. TYPES OF MODELING

Extensive experimental data have been collected in the past 20 years on the CO_2-MEA-H20 system. These data cover thermodynamic equilibrium, rate of absorption and rates of reaction. Among the thermodynamic model, the Kent and Eiselburg method (1976) must be cited for its simplicity. The currently most used model for this system is the Electrolytic NRTL model developed by Chen (1979). It is a model to predict the excess Gibbs energy of a mixture and reproduces experimental data in a wide range of temperature and loadings. The equilibrium data collected by Jou (1995) are used to develop a rate model. The model was developed in ASPEN PLUS with a RATEFRAC module.

Types of modeling used :

1. Thermodynamic model

2. Rate based model

4.2. THERMODYNAMIC MODEL

4.2.1. Solution Chemistry and equilibria

Table 4.1: Thermochemistry in the MEA system [25]

Reaction	**- H (kcal/gmol)**		
	25°C	80°C	120°C
$CO_2(g) \rightarrow CO2$ (aq.)	4.9	2.9	1.3
$CO_2(aq) + H_2O \rightarrow HCO_3^- + H^+$	-2.2	1.7	4.7
$MEA(aq) + H^+ \rightarrow MEA^+$	12.0	12.2	12.1
$MEA(aq) + HCO_3^- \rightarrow MEACOO^- + H_2O$	4.3	5.1	5.4
Overall reaction	18.9	21.9	23.6

4.2.2. Electrolytic NRTL Model

The ENRTL model is a model for the excess Gibbs' free energy of a solution. Activity Coefficient can be related to Gibbs free energy as:

$$\ln\gamma_i = \frac{\partial}{\partial n_i}\left(\frac{G^E}{RT}\right)_{T,P,n_{j\neq i}}$$

Where $G^E = H^E - TS^E$ is the excess Gibbs energy.

The excess enthalpy is determined by the fact that a component changes its interaction with the surrounding components when the composition changes. When ions are present in large amounts in the solution they interact strongly with each other and every molecule of CO_2 among them reduces the intensity of this interaction and so CO_2 is subjected to salting out effect. The excess entropy is due to a change in the randomness of reciprocal position of the molecules in solution. The presence of ions creates a pseudocrystalline structure in the aqueous solution because water molecules tend to hydrate the ions. The ENRTL model assumes that the non ideal entropy of mixing is negligible compared to heat of mixing. The short range molecular forces need to be included to account for hydrogen bonds and local interactions of molecules with ion pairs and ion pairs with ion pairs. It can be described by Non Random Two Liquids theory which uses two assumptions in the presence of ions: Like ion repulsion states that Composition of cations around cations and anions around anions is zero. The local electro-neutrality assumption states that the local charge is always zero.

4.3. RATE BASED MODEL

Even though the involving non-equilibrium reaction is fast, it is not close to equilibrium at absorber conditions. Typical values for stage efficiencies in an absorber tray column are of the order of 0.1-0.2; for packed column around 0.1 for a height of packing of 2-3ft. The various equations that are solved in ASPEN RateSep include [25]:

- Mass and heat balances for the vapor and liquid phases
- Mass and heat transfer rate models to determine interphase transfer rates
- Vapor-liquid equilibrium equations for the interphase
- Estimation of mass and heat transfer coefficients and interfacial areas
- Enhancement of mass and heat transfer processes by chemical reactions

4.3.1. Rate Reactions

Two of the five reactions described in the Thermodynamic model need a kinetic characterisation. There are two possible ways by which CO_2 can react directly in the mixture.

$$CO_2 + MEA + H_2O \xrightarrow{K2,MEA} MEACOO^- + H_3O^+$$

$$CO_2 + OH^- \xrightarrow{K2,OH-} HCO_3^-$$

The first reaction only contributes significantly to the absorption of CO_2. Even if the rate constant of the second reaction is higher than that of first one, the latter is slow due to very small concentration of OH-. It can be non negligible only at rich condition when MEA+ CO_2 reaction is slow.

4.3.2. Mass transfer Modelling in liquid boundary layer

The main mass transfer models are film theory, penetration theory, surface renewal theory and Eddy diffusivity theory among which only Film theory and Eddy diffusivity theory are steady state theory.

- **Film Theory**

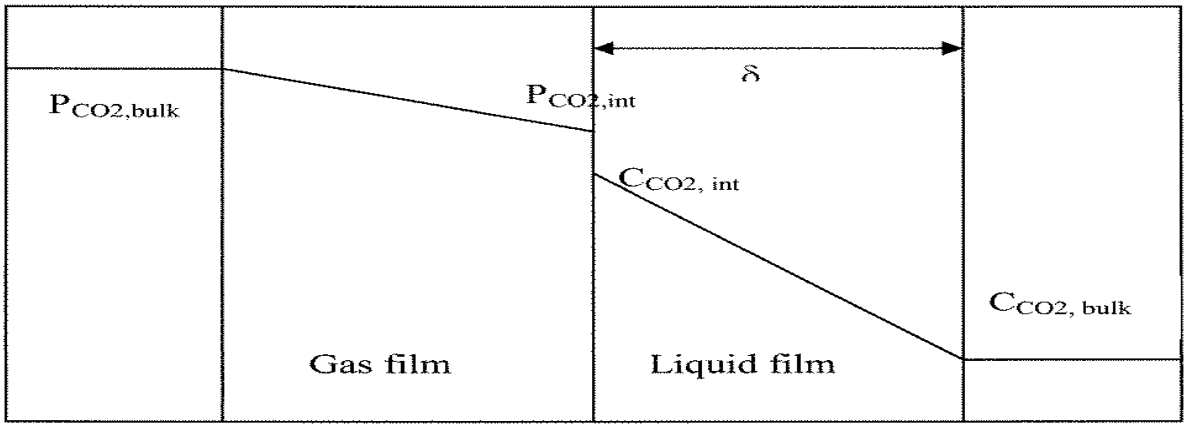

Figure 4.1: Physical absorption representation with film theory [18]

- **Eddy diffusivity theory**

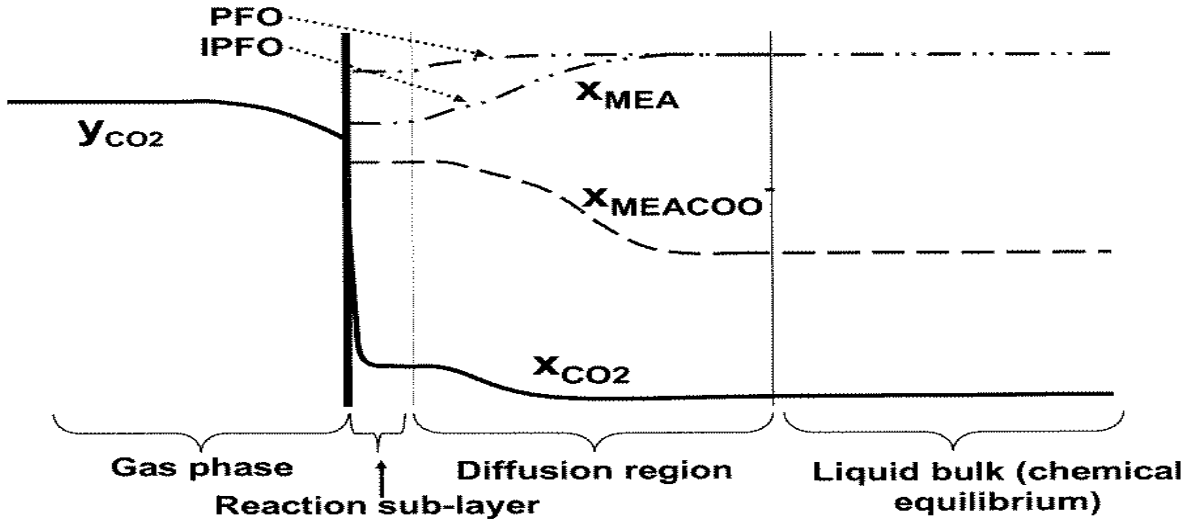

Figure 4.2: Representation of Absorption with fast chemical reaction[18]

4.4. RATEFRAC Kinetic Model

Reaction kinetics, heat transfer coefficient, mass transfer coefficient are used to determine mass transfer and heat transfer rates. RATEFRAC divides the packed column into a user defined number of segments, each corresponding to a given height. The segments are defined to be well mixed in both liquid and gas phase. RATEFRAC doesn't calculate between the interface and the bulk, but the total amount of reaction on a segment averaging reaction rates in the bulk and at interface.

4.5. FILM DISCRETIZATION

ASPEN Rate Sep utilises the Two-Film Theory to accomplish a standard model for heat and mass transfer phenomena on the basis of Film Resistance [18]:

1. **Nofilm:** This signifies the absence of film resistance for the particular phase, thereby ASPEN PLUS performs an equilibrium evaluation as in Themodynamic model.
2. **Film:** It focuses on the diffusion resistance for a film but not on film reactions.
3. **Filmrxn:** It involves the reaction condition factors known as Weighting Factor, which varies between 0 and 1 to calculate phase reaction rates in the film.
4. **Discrxn:** Being the most effective method, it enables the consideration of film reaction; mostly a fast rection. It emphasises on the film discretization into a no. of segments on which the species concentrations and reaction rates are determined at each discrete points to obtain a precise concentration profile.

CHAPTER – 5

DESIGN & SIMULATION

❖ MODELING & COMPARISON

The experimental set up consists of 3 columns: 1 for DCC, 1 for Absorber and 1 for the desorber. The rate model subscribes the RATEFRAC model to be implemented so as to have a clear view of what actually is going on throughout the process. Wherein the absorber and the desorber require the RATEFRAC column model, the DCC is set up using a RADFRAC model. The reason is quite straight forward: the reaction whatever takes place during the process only takes place within the absorber and desorber and these reactions only contribute to the change in characteristics of the /reaction constraints with respect to that occurs in case of the Thermodynamic model. But the DCC only a cooling tower free from reactions.

The thermodynamic model emphasises on the equilibria analysis owing to the fact that it estimates the plate efficiency to be 100% i.e. the vapour and the liquid leaving the tray are in complete equilibrium. However, in actual system this doesn't occur considering there may be some accumulation on each tray, accumulation in the weir, Murphree point efficiency may not be uniform throughout. Again the equilibrium model gives no idea about whether the presence and change in heating medium and heating system affect the process or not. Here, also in practical approach these types of changes directly affect the parameters as the phenomena involving heat transfer such as heat transfer coefficient, dirt factor owing to formation of salts, heat loss through the walls etc. contributes significantly to the reaction condition. Where the thermodynamic model is restricted upto the overall mass balance of the systems, a more practical phenomena concerning the film characteristics, film discretized reaction, mass transfer coefficient and internal reflux criteria can only be encountered with the help of a RATE Model.

Although the thermodynamic model gives us an empirical data regarding the process takes place within the system, the industrial implementation focus on the actual set of data set along with its regression and tolerance so as the project to be implemented. For this, the experimentation must cover every aspect such as the characteristic of the reaction wrt the building height of the absorber and the desorber, the packing material as well as the packing factor dependency, the property estimation data and the propset of the particular stream. The variation of reboiler duty wrt the L/V ratio is another way to analyse the system for the optimal assessment.

The ASPEN PLUS simulation is quite the effective method for the designing and

simulation of a process plant. For CCS process in a laboratory scale, the simulation for the convergence of the data set excels much better performance and time saving as well wrt the other method such as MATLAB and ANCIS etc.

EXPERIMENTAL PROCEDURE

The flowsheet involving the CCS process is to be drawn in the ASPEN PLUS software. For this, the ASPEN PLUS user interface is started and a blank simulation is connected.

❖ DEVELOPING THE FLOW SHEET

The structure consists of 3 columns among which the DCC is to be drawn in RADFRAC model and the Absorber and the Desorber are to be constructed in RATEFRAC model. The Desorber contains a reboiler whereas the other columns don't. The flash is a high pressure separator which separates the water and CO_2; water is recycled to the top of the stripper section after the excess water is purged with the help of a splitter, for which the option FSPLIT is to be commanded. The compressor is a four stage reciprocating compressor, in which in each stage a gradual compressing of the CO_2 takes place and the final outlet is maintained around 90atm. The compressor, so defined, is a MCOMP model that removes the water in a decanting manner through each stage. The pumps and heaters are chosen respectively according to the flowsheet and set in their respective alignment.

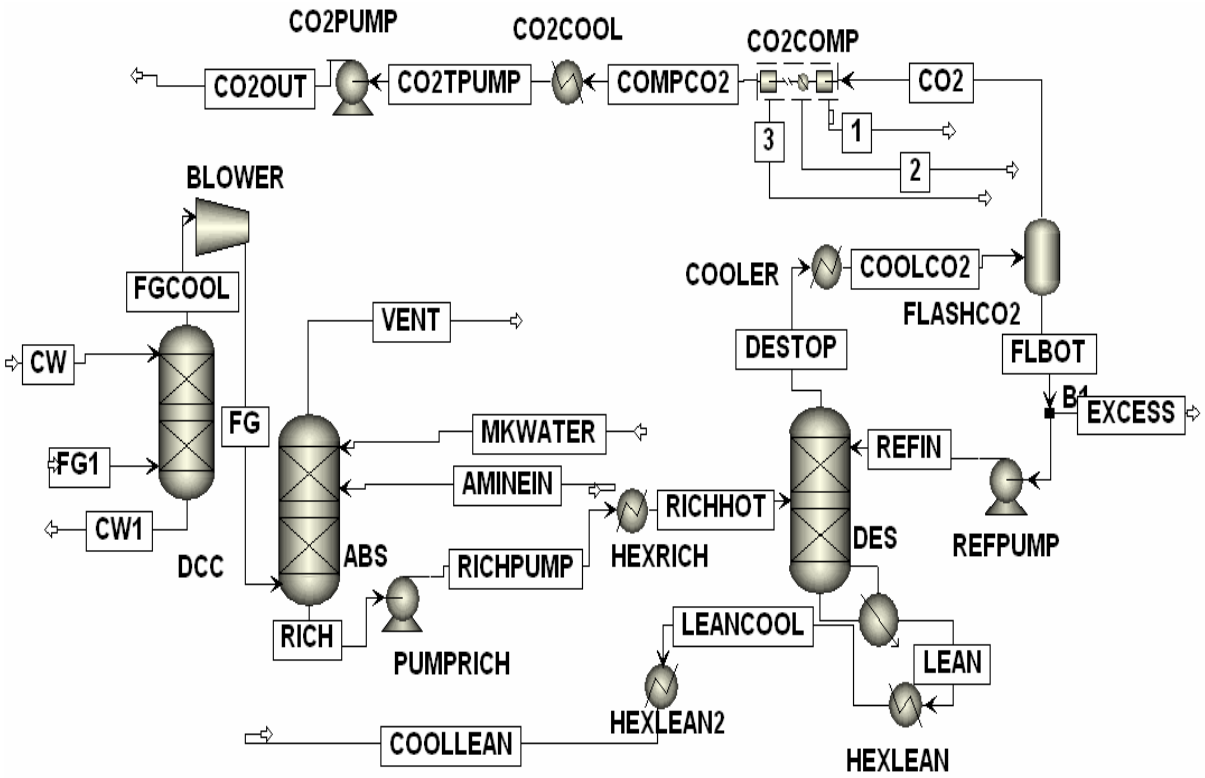

Figure 5.1: Process flow diagram of MEA system as developed in ASPEN Plus [25]

❖ INPUT SPECIFICATION

- The name of the project title and the name of the account is set in the DATA console of the ASPEN PLUS. The components are selected from the ASPEN Data sheet as such:

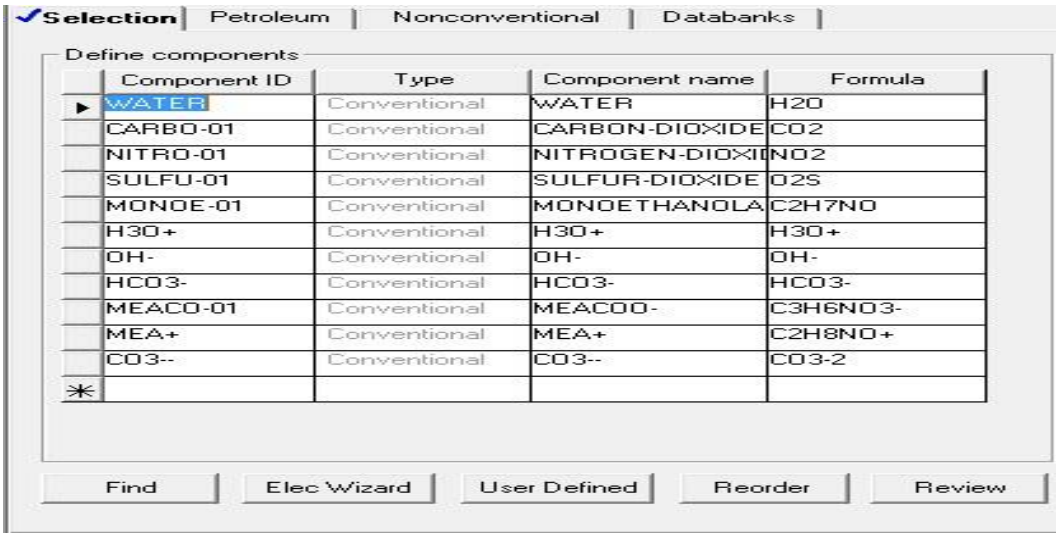

Figure 5.2: Components selected in the ASPEN PLUS Console

- **ELECNRTL** is selected as the property method due to presence of ions in the process.

- **STREAMS**

  Aminein stream is set to have a flowrate of 65kg/hr, a temperature of 45°C, pressure of 1.8 atm and a loading of 0.2. Cooling water and make up water is set to a temperature of 30°C and an appropriate pressure. Flue gas is maintained at a flowrate of 9kg/hr having 10 mol% CO_2 and temperature of 120°C and at 1atm pressure [25].

- **BLOCKS**

  1. **ABSORBER**

     The absorber is set at a pressure of 1.5 atm containing 20 stages with no condenser and reboiler and possesses a typical random packing given as in the table. The packing surface area is taken as 226 sqm/cum and a void fraction of packing is assumed. The temperature estimation for each stage is given as input and other estimates are generated to have a better result. The efficiency is assumed to be Murphree efficiency and the respective stage efficiency are set accordingly.

Table 5.1: Values of parameters used in the absorber for the MEA system [25]

Parameter	Value
Diameter	12 m
Height	17 m
Packing	Norton IMTP Metal 1 in
Lean solvent inlet temperature	40°C

  2. **CO2 COMP**

     It is a four stage isentropic compressor model in which specification from each stage is fixed such as temperature and pressure. The phases of the respective

streams are taken as Total Liquid. The final discharge stream is to be kept at 90atm.

3. HEATERS/ COOLERS

Table 5.2: Different Heaters/Coolers used in the Design along with their specifications

HEATER/COOLER	TEMPERATURE(°C)	PRESSURE (atm)	APPLICATION
CO2COOL	35	90	Cool CO_2 discharged from MCOMP
COOLER	50	1.6	Cool the Desorber top stream
HEXLEAN	60	1.7	Cool the desorber bottom stream
HEXLEAN2	45	1.6	Cool the HEXLEAN outlet stream
HEXRICH	60	2	To heat the absorber bottom to desired temp.

4. PUMPS/BLOWER

Table 5.3: Different Pumps/ Blowers used in the Design along with their specifications

PUMPS	DISCHARGE PRESSURE (atm)	APPLICATION
CO2 PUMP	130	To maintain the liquid phase and long transportation
PUMPRICH	2.2	Facilitating the flow of input stream to the Desorber
REFPUMP	2	Facilitating the flow of recycle stream to the Desorber
BLOWER	1.8	To facilitate the flow to the Absorber

5. **FLASHCO2**

It is a high pressure separator which is maintained at 50C and at a pressure of 1.5 atm where water and CO_2 are seprated.

6. **SPLITTER**

It is a FSPLIT model which removes the excess water with a split fraction of 0.3 for the EXCESS stream.

7. **DESORBER**

The Desorber is typically packed column containing 20 segments along with a kettle reboiler, but no condenser. The reboiler duty is taken as 37.8 MJ/hr and the top segment pressure is maintained at 1.8atm. The packing specification is considered to be a randomly packed column with taking starting segment as 1 and the ending segment as 19. The packing surface area is taken as 226 sqm/cum and a void fraction of packing is assumed. The respective specifications shown below

Table 5.4: Values of parameters used in the desorber of the MEA system [25]

Parameter	**Value**
Diameter	7 m
Height	15 m
Packing	Norton IMTP Metal 1 in
Desorber pressure	1.7 atm
Solvent feed stage	2 (above stage)
Reflux feed stage	1 (on stage)

Again, as with the absorber, for the desorber, also the temperature of the segments are estimated and the other estimated parameters such as vapour and liquid mole fractions are generated in the Estimate Console to have a better result. The efficiency is assumed to be Murphree efficiency and the respective stage efficiency are set accordingly.

❖ CHEMISTRY

The reactions involved in the MEA system are to be specified in the CHEMISTRY console.

$$2\ H_2O \leftrightarrow H_3O^+ + OH^- \qquad (5.1)$$

$$CO_2 + 2\ H_2O \leftrightarrow HCO_3^- + H_3O^+ \qquad (5.2)$$

$$MEA + HCO_3^- \leftrightarrow MEACOO^- + H_2O \qquad (5.3)$$

$$MEA + H_3O^+ \leftrightarrow MEA^+ + H_2O \qquad (5.4)$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \qquad (5.5)$$

The equilibrium constants are temperature dependent as given in (5.6).

$$\ln K_x = A + \frac{B}{T} + C \ln T + DT \qquad (5.6)$$

Table 5.5: Values of temperature dependent parameters for equilibrium constant in MEA system referred from Augsten's work [24].

Reaction	A	B	C	D
(5.1)	132.89	-13445.9	-22.47	0
(5.2)	231.46	-12092.1	-36.78	0
(5.3) (reverse)	-0.52	-2545.53	0	0
(5.4)(reverse)	-3.038	-7008.3	0	-0.00313
(5.5)	216.05	-12431.7	-35.48	0

❖ REACTION

The absorption of CO_2 in MEA, although occurs in the virtue of a rapid reaction, still the reaction constants are hardly close to that obtained through the thermodynamic analysis. So it is a matter of concern to correlate the kinetics of this non-equilibrium system in order to evaluate its dependency with temperature and composition. In this project, two reactions are considered to be occurring during the process as given below [18]:

$$CO_2 + MEA + H_2O \xrightarrow{K2,MEA} MEACOO^- + H_3O^+$$

$$CO_2 + OH^- \xrightarrow{K2,OH-} HCO_3^-$$

The rates of the reactions can be expressed as a 2nd order expression such as [18]:

$$R_{CO2-MEA} = k_{2,MEA}[CO_2][MEA]$$

$$R_{CO2-OH^-} = k_{2,OH^-}[CO_2][OH^-]$$

As always in case of a temperature dependent reaction, both of the above also have Arrhenius expressions.

In order to evaluate the rate of reactions for the above reactions, the following literature data are taken into account. The reactions are generally fast reactions generally involving rapid mixing and so the respective data are taken from the table.

Table 5.6: Some literature data on the reaction between CO_2 and aqueous MEA [18]

Reference	T range (^{0}K)	[MEA] (M)	$k_{298\ K}$	E_A kJ/mol	Experimental technique
Clarke (1964)	298	1.6-4.8	7500		Laminar jet
Danckwerts And Sharma (1966)	291-308	1.0	7600, 6970	41.8	Laminar jet
Hikita et al. (1977)	278-315	0.015-0.18	5868	41.2	Rapid mixing
Alvarez-Fuster et al. (1980)	293	0.2-2.0	5750		Stopped flow
Penny and Ritter (1983)	278-303	0.009-0.06	4990	42.2	Stirred cell
Littel et al. (1992)	318-333		3703		

❖ DESIGN SPECIFICATION

1. **Vent CO_2**

   The absorber comprises of a design specification that controls the CO_2 which is allowed to vent from absorber. The required capture capacity is attained by varying the amine flow rate into absorber. The method starts with selecting a DS-1 in which a variable VENT is defined followed by specifying the Specs at 1.2 with a tolerance of 0.02. The design specification is completed with the varying variable AMINEIN which is varied from a flow rate of 40kg/hr to 100kg/hr.

2. **Reboiler Duty**

   The important concern is the recycling of the regenerated Amine for which the property of COOLLEAN is to be made equivalent as that of the AMINEIN stream. This facilitates a close loop convergence for which, the loading of the two streams are to be equivalent. In the Prop-sets Console, two property-sets FAPPCO2 and

FAPPMEA are selected and the appropriate phase is to be specified. FAPP denotes the apparent flow rates of the two streams and their ratio is the loading.

In the Design Specification Console of the Desorber, the prop sets are defined and the loading is set at 0.2. in the vary tab, the reboiler duty is varied from 30 to 50 MJ/hr.

3. **Cross-exchanger duty**

The cross heat exchanger is the combination of HEXRICH and HEXLEAN so that a closed loop won't be created. The heat duties of the two heat exchangers need to be equivalent for an effective functioning as a cross-heat exchanger.

The heat duty of the HEXLEAN is set same as the negative heat duty of the HEXRICH ie the sum of the two heat duties are made zero in the Spec tab and some tolerance is given. The AMINEIN flow rate is varied to avail the simulation.

4. **Cross-exchanger approach temperature**

Apart from the matching of the cross heat exchanger, another design specification on the approach temperature for the cross heat exchanger is recommended. For this, the temperature of HEXLEAN outlet is maintained at 10°C above the temperature of the HEXRICH inlet.

In the DS-3 console, the two streams are defined and the specs tab set the temperature difference of the two streams as 10°C. The simulation is to be converged with varying the Aminein Flow rate.

5. **Water balance**

The closed loop convergence is ensured with the simulation of the water balance, which is specified in DS-4 console. The total mass flow in of the water is matched with the total mass of water outflow in the system. This is attained by varying the Makeup Water flow rate to absorber. The flow of CW, CW1, MKWATER, 1, 2, 3 are to be mentioned for this in the Define tab.

CHAPTER-6

OBSERVATION & DISCUSSION

After the ASPEN PLUS simulation is completed, the characteristics, composition and specification of each streams is analysed from the result sheet. The Block calculation also gives the required parameters which can be further utilised for comparison and design analysis. In the rate model, the study of the variation of CO_2 out with No. of Film Segment, variation of reboiler duty with other flow parameters, Effect of the absorber and desorber height on the loading, Effect of solvent temperature on the Design specified constraints, Effect of packing material and area on the CO_2 capture, variation of CO_2 with loading, effect of temperature of the column on the mass transfer coefficients, effect of the reboiler duty on the heat transfer coefficient, the cost optimisation and the parameter sensitivity can be accomplished. Yet, amongst all the above set of rigorous correlations, some of the correlations are within the scope of the project.

6.1. Effect of the no. of segments on the amount of CO_2 captured

Since in the MEA system, the Discrxn option is chosen for the liquid film due to occurrence of fast reaction and Film option is chosen for the vapour film due to no reactions. Thus, relatively more discretization Points should be allotted at the film boundary. As the implementation of any project depends on the accuracy of the result and the cost factor, No. of the discretized points requires to be optimised. Beyond certain points, the increase in no. of discretized points doesn't improve the capture, however, ends up increasing the computational time, which in turn affects the cost factor.

For the determination of the optimal no. of points, a no. of simulations is to be performed with the different set of no. of discretized point and CO_2 escaped from absorber was noted and a plot was drawn between the number of discretization points and CO_2 out.

Table 6.1: Specified discretization points in the liquid film

Point	Non-dimensional distance from vapor side in the liquid film
1	0.001
2	0.005
3	0.01
4	0.05
5	0.1
6	0.15
7	0.2
8	0.3

RESULT TABLE:

Table 6.2: The variation of CO_2 *out with the change in no. of Discretized Points*

No. of Discretized Points	CO_2 Out (kg/hr)
1	0.13
2	0.23
3	0.34
4	0.46
5	0.55
6	0.64
7	0.641
8	0.641

PLOTTING OF THE RESULT:

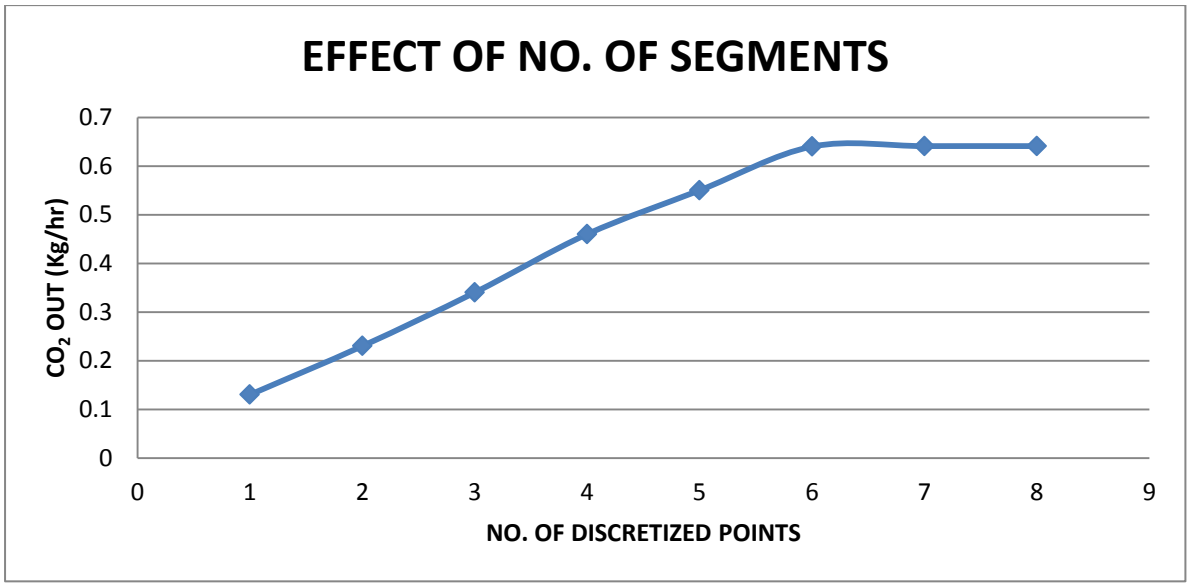

Figure 6.1: Effect of the no. of segments on the CO2 out

DISCUSSION:

The plot shows the increase in the CO_2 out until 6 discretization points owing to the fact that the lower discretization points evaluates a vague high reaction rate in the segments due to generation of an erroneous concentration profile. After 6 points, the accurate and optimum result is achieved and beyond this, the solution will be time consuming unnecessarily.

6.2. Variation of reboiler duty and rich loading with L/G for 80% CO_2 capture

The ASPEN PLUS Constraints Console set the CO_2 capture as 80% and with the change in reboiler duty respective molar rates of the liquid and vapour going out of the desorber is determined. The ratio of the molar flow rate of CO_2 to molar flow rate of MEA in the outlet stream through the desorber bottom is defined as the Lean Loading whereas the loading of the outlet stream of the absorber is denoted as Rich Loading. Now, the results available from the simulation is organised in a tabulated form and the relation between Reboiler Duty vs L/G Ratio and the relation between Loading vs L/G Ratio are plotted.

RESULT TABLE:

Table 6.3: The variation of Reboiler Duty and Loadings with the change in L/G Ratio

L/G RATIO	REBOILER DUTY (KJ/Kg)	LEAN LOADING	RICH LOADING
0.8	7800	0.1	0.5
1	6200	0.125	0.5
1.2	5100	0.16	0.5
1.4	4500	0.2	0.5
1.6	4200	0.24	0.5
1.8	3950	0.27	0.5
2	3800	0.3	0.5

PLOTTING OF THE RESULT:

(a) Effect of L/G Ratio on Reboiler Duty

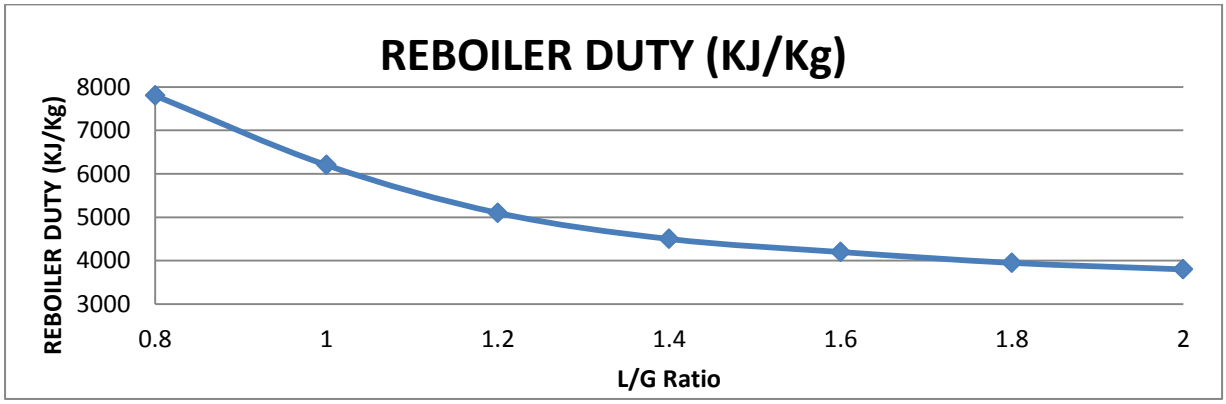

Figure 6.2: Effect of L/G Ratio on Reboiler Duty

(b) Effect of L/G Ratio on Loading

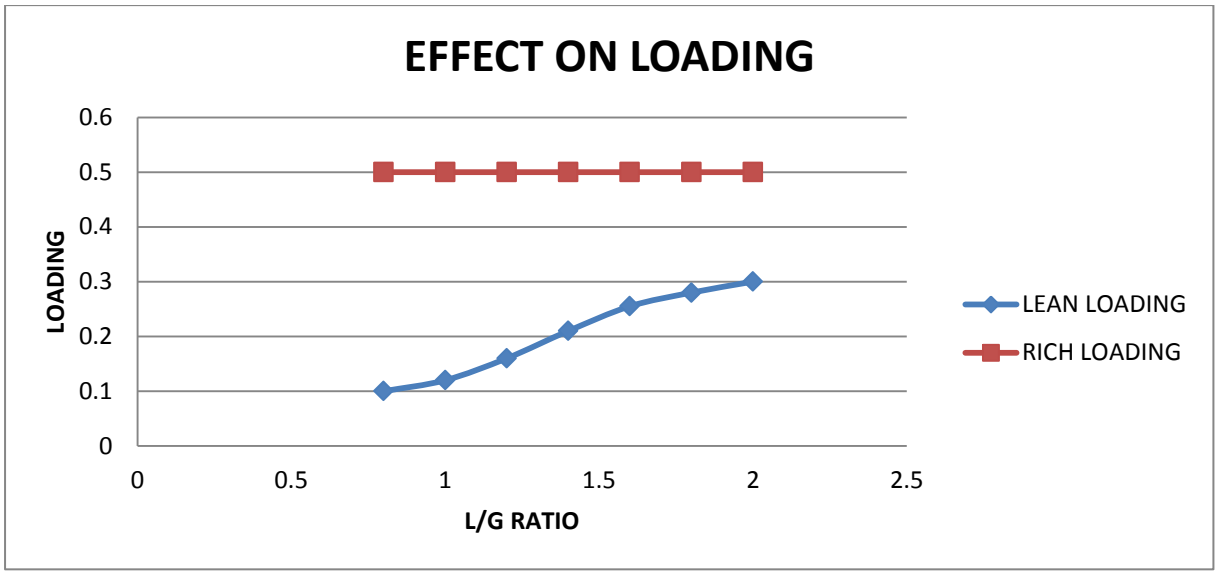

Figure 6.3: Effect of L/G Ratio on the respective loadings

DISCUSSION:

The reboiler duty is observed to decrease with increase in L/G Ratio. Initially it is very high due to the requirement of large amount of Amine Solution to strip the CO_2 present in the system and so a higher quantity of steam is also to be produced resulting in higher reboiler duty. As the lean loading increases with the L/G Ratio, the amount of steam required for stripping decreases resulting in lower reboiler duty for a 80% capture. Hence, an optimisation w.r.t. lean loading needs to be determined.

6.3. Effect of Absorber height on Reboiler Duty for 80% CO_2 capture

The ASPEN PLUS Constraints Console set the CO_2 capture as 80% and with the change in Absorber height the respective reboiler duty is determined. The sensitivity analysis of the parameters generated the following data:

RESULT TABLE:

Table 6.4: Variation of reboiler duty with absorber height for 80% CO_2 capture

HEIGHT OF THE ABSORBER (m)	REBOILER DUTY (MJ/hr)
15	38
18	36.32
21	35.16
24	34.29
27	33.93
30	33.81
33	33.76
36	33.75

PLOTTING OF THE RESULT:

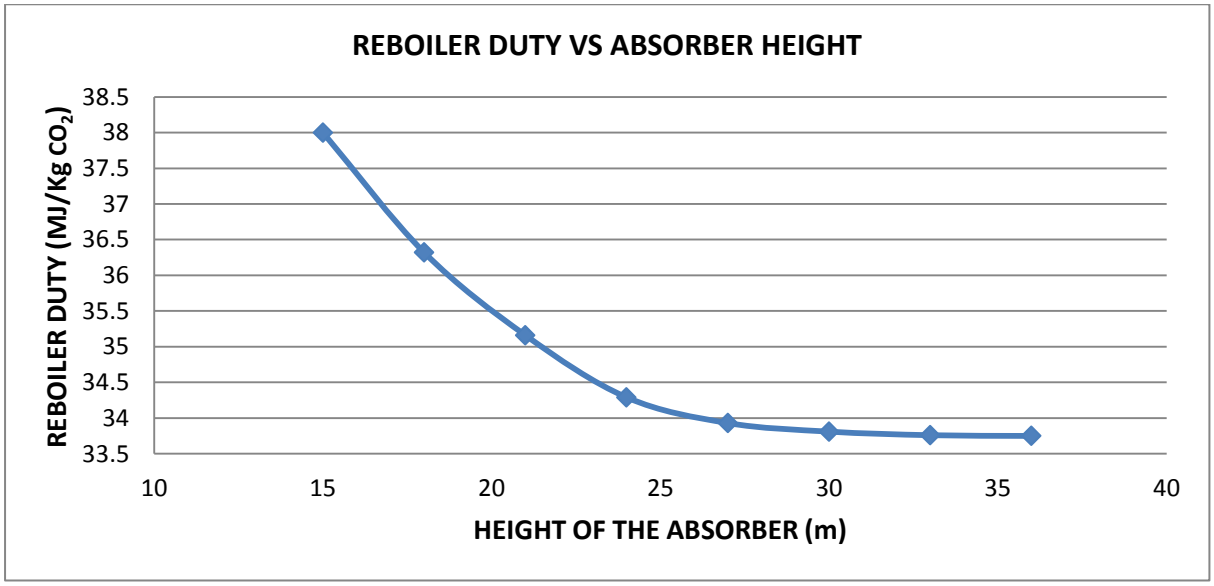

Figure 6.4: Effect of absorber height on Reboiler Duty

DISCUSSION:

The reboiler duty is found to decrease with increase in Absorber height until a particular height and then tend to remain constant or rather not change much. The reason is due to with increase in height, the total packing surface area provided increases and the rich loading also tends to decrease. Thus, a less amount of steam can manage to perform the operation, thereby reduces the reboiler duty. However, with increase the height further, the rich loading remains constant and the minimum reboiler duty can’t be altered and so the reboiler duty mostly remains constant. But the cost factor is accompanied with the change in height, thus optimisation on basis of cost is much required for determining the optimal absorber height.

6.4. Effect of Desorber height on Reboiler Duty for 80% CO_2 capture

The ASPEN PLUS Constraints Console set the CO_2 capture as 80% and with the change in Desorber height the respective reboiler duty is determined. The sensitivity analysis of the parameters generated the following data:

RESULT TABLE:

Table 6.5: Effect of Desorber height on Reboiler Duty for 80% CO_2 capture

HEIGHT OF THE DESORBER (m)	REBOILER DUTY (MJ/ hr)
12	37.5
15	36.29
18	35.33
21	34.67
24	34.15
27	33.94
30	33.87

PLOTTING OF THE RESULT:

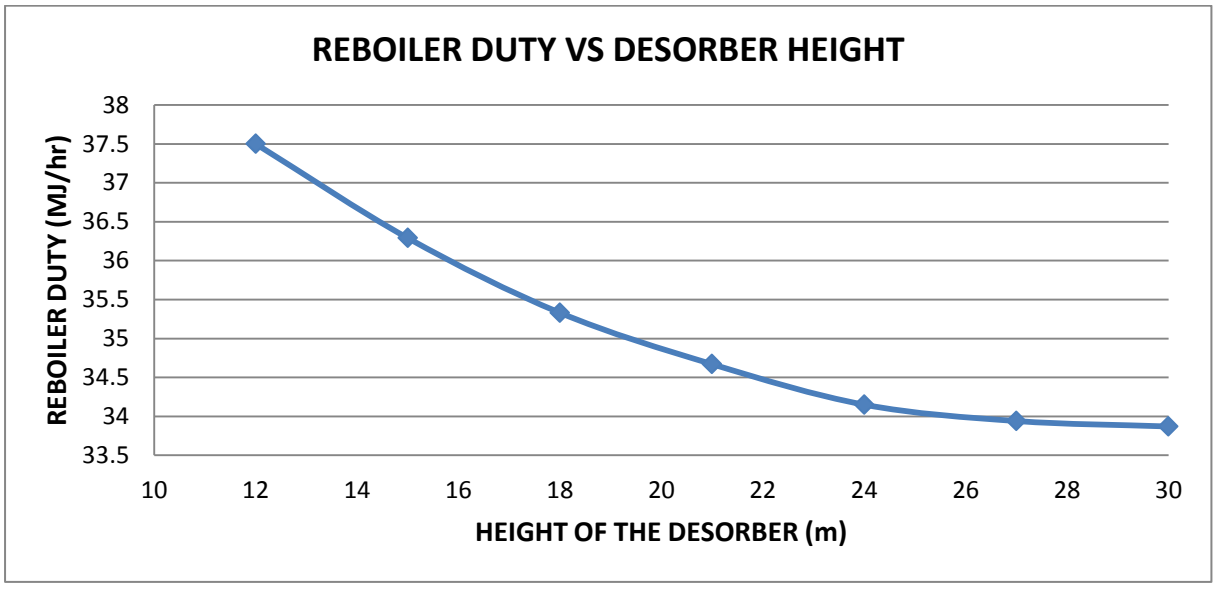

Figure 6.5: Effect of Desorber Height on the Reboiler Duty

DISCUSSION:

The reboiler duty is found to decrease with increase in Desorber height until a particular height and then tend to remain constant or rather not change much. The reason is due to with increase in height, the total packing surface area provided increases which generally facilitates the desorption process. Thus, a less amount of steam can manage to perform the operation thereby reduces the reboiler duty. However, with increase the height further, the minimum reboiler duty can't be altered and so the reboiler duty mostly remains constant. But the cost factor is accompanied with the change in height, thus the optimisation on the basis of cost is much required for determining the optimal desorber height.

6.5. Effect of solvent temperature & Absorber Temperature Profile

With decrease in the absorber temperature, the rate of reaction and diffusivity of the respective components tend to decrease. Thus, simulations are obtained at different Amine temperatures of 30, 40 and 50°C. However, the reboiler duties mostly remain constant in spite of the change in temperature of the Amine owing to a low specific heat of the solvent. But the change in solvent temperature can affect the temperature profile of the absorber.

RESULT TABLE:

Table 6.6: Absorber Temperature Profile

FRACTIONAL HEIGHT FROM THE ABSORBER TOP	ABSORBER TEMPERATURE (°C)
0.05	45
0.1	48
0.15	50
0.2	49
0.25	48.3
0.3	47.8
0.35	47.4
0.4	47.1
0.45	46.8
0.5	46.6
0.55	46.4
0.6	46.2
0.65	46
0.7	45.82
0.75	45.7
0.8	45.6
0.85	45.6
0.9	45.6
0.95	45.6
1	45.6

PLOTTING OF THE RESULT:

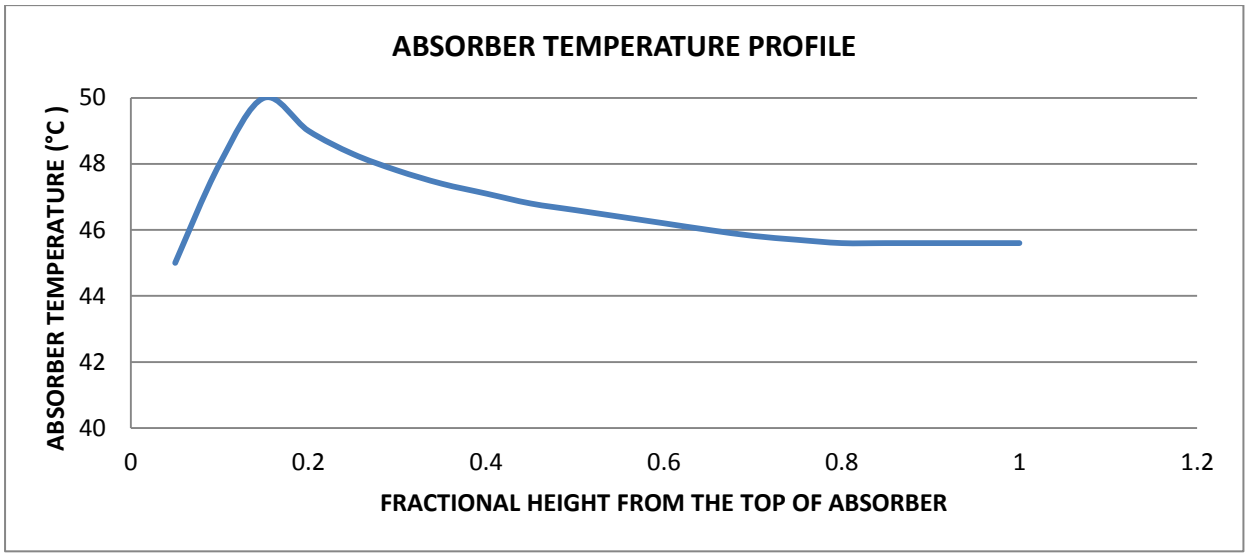

Figure 6.6: Absorber Temperature Profile

DISCUSSION:

The figure shows a rise in temperature at the top section of the absorber and then it is decreased to the operating temperature as we move down the column and finally maintained at that temperature. The reason is mainly the reaction occurs at the top section, mainly on the 2nd segment where the Amine solution enters. As the reactions are highly exothermic, the released heat is absorbed by the liquid and its temperature increases owing to its low specific heat. However, by exchanging heat with the gas, the temperature is noticed to be decreased in the subsequent sections.

6.6. Effect of desorber pressure

The characteristics of CO_2 capture at different Desorber Pressure are highly essential to optimise the reaction condition throughout the process. Also the cost factor for different pressure is different due to the involvement of costly high pressure steam. Thus, Desorber Pressure is varied to evaluate the change of Reboiler Duty and the Desorber Temperature.

RESULT TABLE:

DESORBER PRESSURE (atm)	REBOILER DUTY (MJ/hr)	DESORBER TEMPERATURE (°C)
1.6	39.29	90
1.8	37.23	102
2	35.66	115
2.2	34.73	127
2.4	34.17	137
2.6	33.86	144
2.8	33.75	148
3	33.72	150

Table 6.7: Variation of Desorber Pressure on Reboiler Duty and Desorber Temperature

PLOTTING OF THE RESULT:

(a) EFFECT OF DESORBER PRESSURE ON DESORBER TEMPERATURE

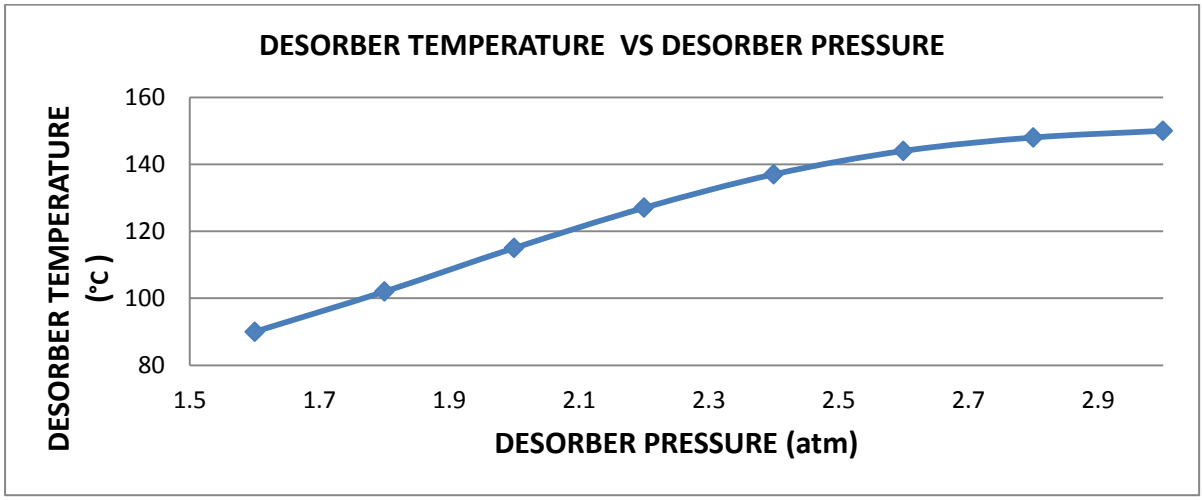

Figure 6.7: Effect of Desorber Pressure on Desorber Temperature

(b) EFFECT OF DESORBER PRESSURE ON REBOILER DUTY

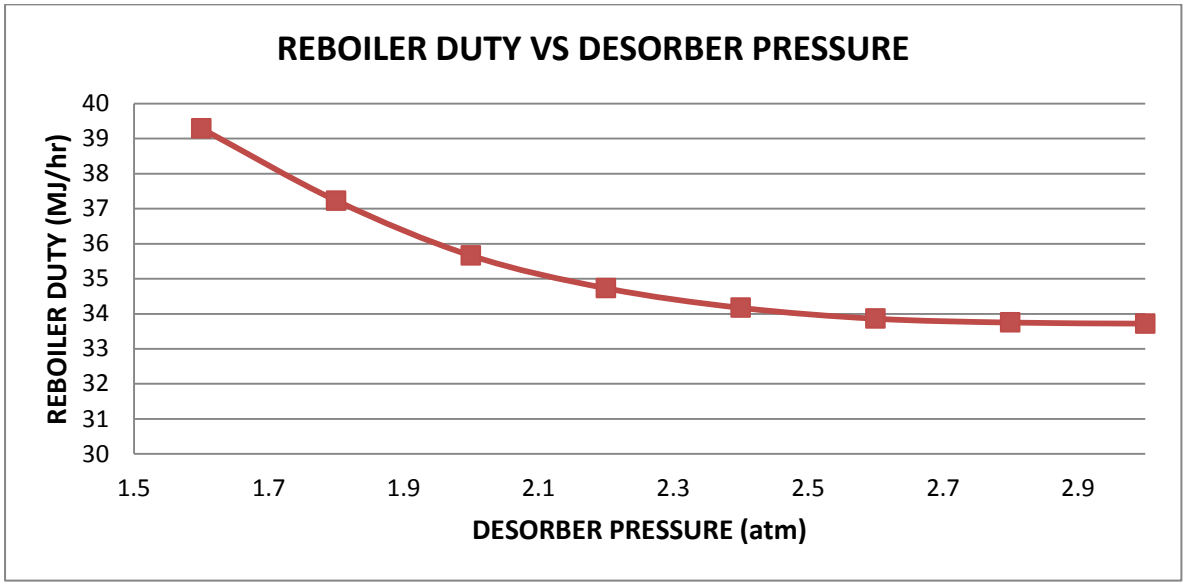

Figure 6.8: Effect of Desorber Pressure on Reboiler Duty

DISCUSSION:

With the increase in pressure, the temperature of the desorber column is increased as expected and stripping of CO_2 to gas phase is favoured although at presence of a lower amount of steam. Thus, it is advantageous to envisage a comparatively high pressure in the desorber but at the same time can't ignore fact that it may lead to the degradation of MEA.

6.7. Effect of cross-heat exchanger approach temperature

The working potential of cross-heat exchanger is entitled to its approach temperature especially on cold side [26]. The factors for calculating the heat transfer coefficient are more dependent on the cold side temperature and surface area than on that of the hot side due to the lower in the value of the sensible heat capacity on the cold side.

RESULT TABLE:

Table 6.8: Variation of Reboiler Duty at different Cross Heat Temperature Approach

LEAN LOADING	REBOILER DUTY(MJ/hr) FOR 5°C CROSS HEAT APPROACH	REBOILER DUTY (MJ/hr) 10°C CROSS HEAT APPROACH
0.1	48.52	48.52
0.14	43.11	43.11
0.18	39.55	40.46
0.2	37.6	37.8
0.22	37.24	38.74
0.26	37.46	39.64
0.3	38.07	41.28

PLOTTING OF THE RESULT:

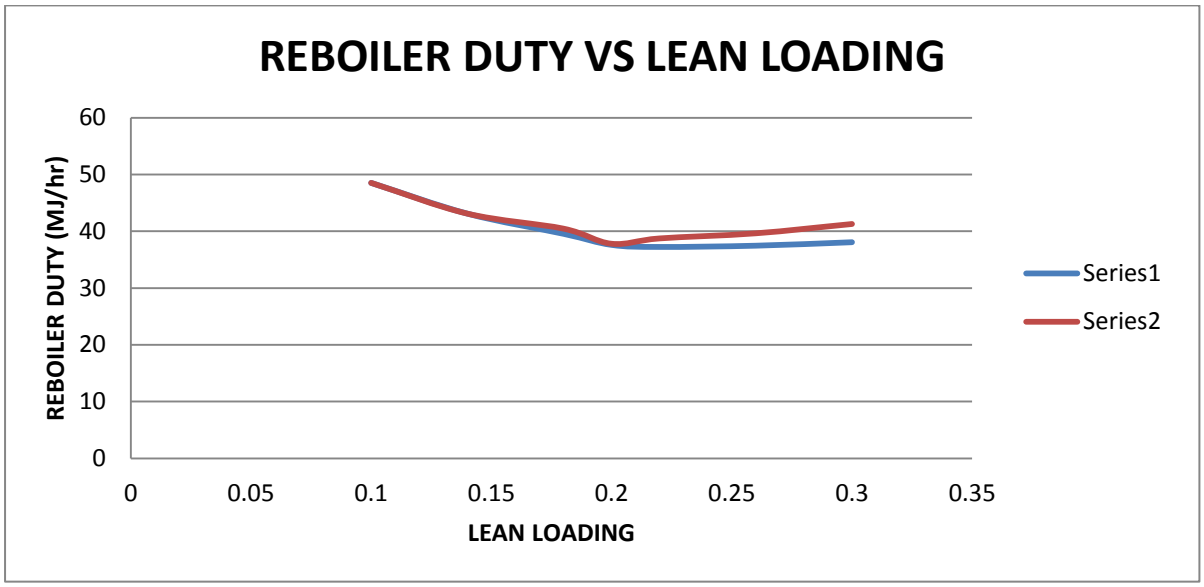

Figure 6.9: Variation of Reboiler Duty at different Cross Heat Temperature Approach

DISCUSSION:

If this approach temperature can be reduced lower than what we have considered in the base simulation, it will result in lowering of the sensible heat requirements but at the same time may result in the higher load in the subsequent equipment. The reboiler duty is reduced around 7% with the approach temperature decreasing from 10°C to 5°C, but to ensure the acceptance of low approach temperature, a cost optimisation is required.

6.8. Effect of packing

ASPEN Rate Model emphasises on involvement of both random and structured packing in both columns, which affects the reboiler duty by the virtue of different surface area of the respective packings. The random packing was analysed for the Norton IMTP Metal 25 mm packing whereas the structured packings were taken into consideration for the Sulzer MellaPak 752Y packing and the SuperPak Metal 300 packing. [25]

Table 6.9: Minimum reboiler duty obtained with different packings in the absorber [25]

Packing	SA (sqm/cum)	Rich Load	Reboiler Duty (kJ/kg CO_2)
IMTP Norton 25 mm	226	0.491	4292
SuperPak Metal 300	300	0.498	4219
MellaPak Sulzer 752Y	495	0.504	4152

RESULT TABLE:

Table 6.10: Effect of Lean Loading on different Packing Material

LEAN LOADING	REBOILER DUTY (MJ/hr)

	IMTP	SUPER PAK	MELLAPAK
0.1	48.52	46.31	44.76
0.14	43.11	41.4	40.01
0.18	38.57	37.32	36.25
0.2	37.8	36.11	35
0.22	38.17	35.46	34.15
0.26	38.74	35.13	33.97
0.3	39.31	34.97	33.80

PLOTTING OF THE RESULT:

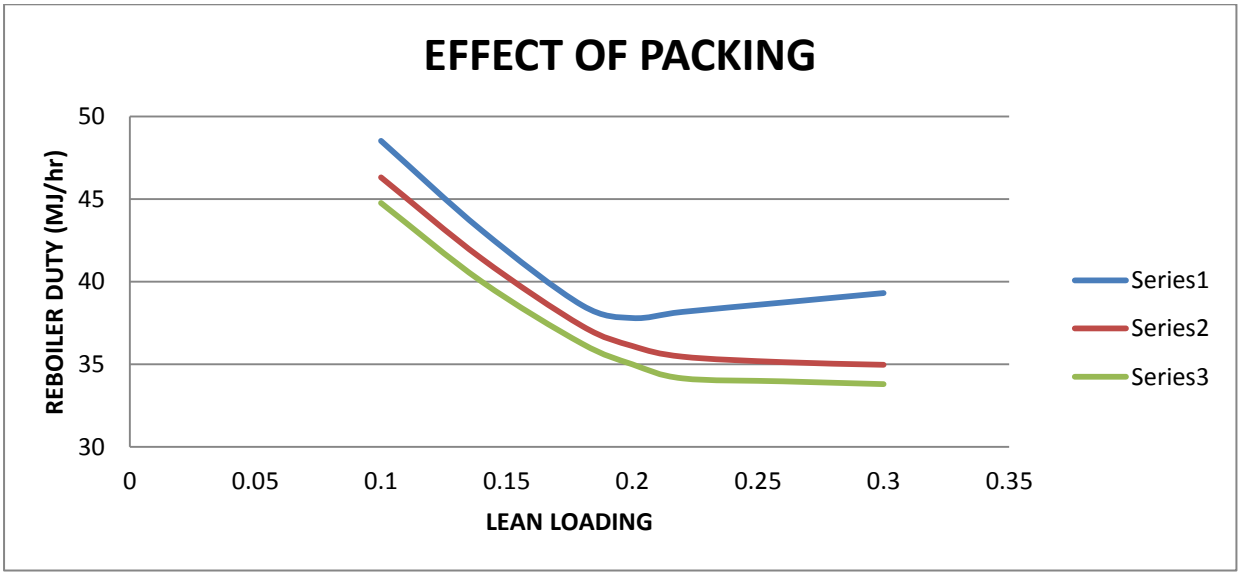

Figure 6.10: Effect of Lean Loading on different Packing Material

DISCUSSION:

The higher the extent of stripping in the desorber column, the lower is the amount of Lean loading and vice versa. Thus, with the increase in lean loading of the solvent, the stripping tendency decreases which ensures a reduction in the amount of steam required for stripping and in turn the reboiler duty decreases as obtained from the Result Table for each of packing material. Now, the Table 6.9 shows the respective surface area for different packing. The higher of surface area enables high contact with the packing material, which increases the mass transfer coefficient for the system and so the stripping efficiency increases. As the stripping efficiency increases, it eases the separation process and results in decrease in required reboiler duty. Thus, with increase in lean loading and increase in Surface area, the Reboiler duty should decrease as obtained from the plot.

CHAPTER-7

CONCLUSION & FUTURE SCOPE OF WORK

CONCLUSION

I can hereby conclude that for simulation and design of a CO_2 capture unit using MEA, we need to carefully visualise the actual process going on and to understand what different parameters are required for successfully getting the results for which an equilibrium analysis is first needed to estimate the bound of any parameter. Again, the simulation of such complicated problems are prone to erroneous result, thus a systematic approach on the analysis along with patience is a must.

The RATE model analysis reported a satisfied and mostly correct result free from errors. The variation of the RATE model w.r.t the Thermodynamic Model was reviewed on the basis of the result. Due to the consideration of mass transfer, heat transfer, solution kinetics and interface effect as well as the chemical kinetics and film discretization, the actual process occurring throughout the system could be explained. The dependency analysis of the CO_2 capture on the reboiler duty, lean loading, the packing characteristics and the column height was sufficient to have a complete Simulation & Designing of this CCS project work. However, to gain an idea on the overall phenomena, Optimisation, Sensitivity, Property Analysis study need to be incorporated.

FUTURE SCOPE OF WORK

In thermodynamic model, the absorber and desorber column were designed as a set of stages, with each stage in equilibrium and the plate efficiency was assumed to be 100%. Hence, these simulations present the most optimistic results attainable and these values exhibit a maximum value that can be attained in the process.

After the results of the equilibrium model were attained, the rate based modelling was incorporated on the basis of those data just like in a Simulation Mode. The rate model result data that obtained in the prescribed input specification and design specification although is mostly accurate; still the validity of those specifications must be examined. For example: Suppose a desorber of height 200m gives the best set of results for a simulation, but the feasibility of this height is impossible considering the civil engineering work and the cost factor. Thus, an optimisation analysis of the model is a must for a project to be implemented.

Apart from, the data plotting, a data correlation and data regression also need to be analysed to have a clear view of the variation of the data from point to point. Pump around option need to be considered to have a better internal heat transfer and reduction in the load on the condenser. Different Property Analysis can also be observed and the simulation for the other solvents can be incorporated and a comparison study can be accomplished. Also, the sensitivity analysis for different extent of capture can be evaluated. The Case Study on different set of parameters will no doubt give us a better improvement on the result.

REFERENCE

[1] Energy Information Administration, *Electric Power Annual 2007: A Summary*. 2009: Washington, D.C.

[2] Energy Information Administration, *International Energy Outlook*. 2009: Washington, D.C.

[3] "Glossary of climate change acronyms". UNFCCC. Retrieved July 15, 2010

[4] Hagg, M.B. and A. Lindbrathen, *CO2 capture from natural gas fired power plants by using membrane technology*. Industrial & Engineering Chemistry Research, 2005.

[5] Bounaceur, R., N. Lape, D. Roizard, C. Vallieres, and E. Favre, *Membrane processes for post-combustion carbon dioxide capture: A parametric study* Energy, 2006.

[6] Clarke, D.e.a., *CO2 Capture and Storage - A VGB Report on the State of the Art*. 2004.

[7] Hongyi Dang; **CO2 Absorption Rate and Solubility in Monoethanolamine /Piperazine/ Water;** *First National Conference on Carbon sequestration, Washington, DC, May 14-17, 2001*

[8] Strazisar, Anderson, White; Degradation of MEA used in CO2 capture from Flue gas of a Coal fired Electric Power Generating System

[9] Andrane, Zaparoli; A survey on the CO2 capture technologies from power plant Flue gases

[10] Dillon, D.J., Panesar, R.S., Wall, R.A., Allam, R.J., White, V., Gibbons, J., and Haines, M.R., *Oxy-Combustion Processes for CO2 Capture From Advanced Supercritical PFand NGCC Power Plant*, in *7th International Conference on Greenhouse Gas Control Technologies*. 2004: Vancouver, Canada.

[11] Wilkinson, M.B., J.C. Boden, T. Gilmartin, C. Ward, D.A. Cross, R.J. Allam, and N.W. Ivens. *CO2 capture from oil refinery process heaters through oxyfuel combustion*. In *Sixth International Conference on Greenhouse Gas Control Technologies*. 2002. Kyoto, Japan: Elsevier Science Ltd, Oxford UK.

[12] Strömberg, L., G. Lindgren, J. Jacoby, R. Giering, M. Anheden, U. Burchhardt, H. Altmann, F. Kluger, and G.-N. Stamatelopoulos, *Update on Vattenfall's 30 MWth oxyfuel pilot plant in Schwarze Pumpe.* Energy Procedia, 2009

[13] Dyer, P.N., R.E. Richards, S.L. Russek, and D.M. Taylor, *Ion transport membrane technology for oxygen separation and syngas production.* Solid State Ionics, 2000

[14] Herzog, H., J. Meldon, and A. Hatton, *Advanced Post-Combustion CO2 Capture*. 2009.

[15] Le Thiez, P., G. Mosditchian, T. Torp, P. Feron, I. Ritesma, P. Zweigel, and E. Lindberg. *An innovative European integrated project: CASTOR - CO2 from capture to storage*. in *Seventh International Conference on Greenhouse Gas Control Technologies*. 2004. Vancouver, Canada.

[16] Wald, M., L., *Refitted to Bury Emissions, Plant Draws Attention* in *The New York Times*. 2009: New York.

[17] Rochelle, G.T., *Amine Scrubbing for CO2 Capture.* Science, 2009

[18] Freguia, S., *Modeling of CO2 Removal from Flue Gases with Monoethanolamine*, in *Chemical Engineering*. 2002, University of Texas at Austin: Austin.

[19] Idem, R., M. Wilson, P. Tontiwachwuthikul, A. Chakma, A. Veawab, A. Aroonwilas, and D. Gelowitz, *Pilot plant studies of the CO2 capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO2 capture technology development plant and the Boundary Dam CO2 capture demonstration.* Industrial & Engineering Chemistry Research, 2006.

[20] Sartori, G. and D.W. Savage, *Sterically hindered amines for carbon dioxide removal from gases.* Industrial & Engineering Chemistry Fundamentals, 2002.

[21] Aroonwilas, A. and A. Veawab, *Characterization and comparison of the CO2 absorption performance into single and blended alkanolamines in a packed column.* Industrial & Engineering Chemistry Research, 2004.

[22] Tosh, J.S., J.H. Field, H.E. Benson, and W.P. Haynes, *Equilbirium Study of the System Potassium Carbonate, Potassium Bicarbonate*

[23] Yeh, A.C. and H.L. Bai, *Comparison of ammonia and monoethanolamine solvents to reduce CO2 greenhouse gas emissions.* Science of the Total Environment, 1999

[24] Augsten, D.M., *A model for vapor-liquid equilibria for acid gas-alkanolamine- H_2O systems*, in *Chemical Engineering*. 1989, University of Texas at Austin: Austin.

[25] Anusha Kothandaraman; Carbon Dioxide Capture by Chemical Absorption: A Solvent Comparison Study; MASSACHUSETTS INSTITUTE OF TECHNOLOGY, JUNE 2010

[26] Tobiesen, F.A., H.F. Svendsen, and K.A. Hoff, *Desorber Energy Consumption Amine Based Absorption Plants.* International Journal of Green Energy, 2005(2).